Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica C 415 (2004) 125–132
PHYSICA C
www.elsevier.com/locate/physc

A new technique for the growth of epitaxial YBCO using spray pyrolysis

Vyacheslav F. Solovyov [a,*], Harold J. Wiesmann [a], Li-Jun Wu [a], Masaki Suenaga [a], Kartik Venkataraman [b], Victor A. Maroni [b]

[a] Department of Materials Science, Brookhaven National Laboratory, 76 Cornell Avenue, Upton, NY 11973, USA
[b] Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

Received 21 June 2004; received in revised form 23 July 2004; accepted 16 August 2004

Abstract

A new technique for the growth of epitaxial *c*-axis oriented $YBa_2Cu_3O_7$ using spray pyrolysis at atmospheric pressure is described. The technique consists of three steps: the deposition of an oxide precursor by spray pyrolysis of a nitrate solution, fluorination of the oxide precursor in an atmosphere containing a fluorinated gas, and finally, growth of $YBa_2Cu_3O_7$ by the conventional ex situ process. The microstructure of both the oxide and fluorinated precursor is described along with data on the rate of fluorination. We have routinely achieved critical currents of 0.5 MA/cm^2 for 1 μm thick films at 77 K in self-field.

PACS: 74.76.Bz; 81.15.Np
Keywords: YBCO; Coated conductors; Barium fluoride process; Spray pyrolysis

1. Introduction

The preparation of $YBa_2Cu_3O_7$ using the so-called ex situ barium fluoride process [1,2] allows reproducible growth of epitaxial *c*-axis oriented $YBa_2Cu_3O_7$ (YBCO) layers at temperatures below 800 °C. This approach has been extensively studied for application in YBCO coated conductor development [3,4]. The process requires a fluorinated precursor deposited on an oriented substrate. The precursor usually consists of an intimate stoichiometric mixture of BaF_2, Cu, Y, where Cu and Y may be in form of oxides or fluorides or a combination thereof. There are two mainstream techniques for depositing such a precursor, vacuum deposition [5] and coating a substrate with a trifluoroacetate (TFA) metalo-organic solution [6,7]. Though quite different in detail, both

* Corresponding author. Tel.: +1 631 3445437; fax: +1 631 3444071.
E-mail address: solov@bnl.gov (V.F. Solovyov).

0921-4534/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.physc.2004.08.006

techniques produce a fluorinated precursor, where Ba and Y are present as an oxy-fluoride or fluorides and Cu is in the form of CuO. These BaF_2 processes are of great interest for the fabrication of so-called YBCO coated conductors for electric power devices and high magnetic field applications.

During ex situ processing, the YBCO growth initiates at the substrate. As the growth proceeds the epitaxial YBCO–precursor interface uniformly advances towards the film surface. Epitaxy can be achieved in thick (>1 μm) YBCO films at low temperatures from vacuum deposited precursors [5,8]. This is believed to occur via the presence of a liquid phase containing Y, Ba, Cu and oxygen at the epitaxial YBCO–precursor interface, which dramatically enhances the mobility of the precursor atoms [9,10].

We propose an alternative method of preparing the fluorinated YBCO precursor, which may be more economical than the two mainstream ex situ routes described above. In this process, an aqueous yttrium, barium, copper nitrate salt solution is prepared. Then the salt solution is used to deposit a un-fluorinated oxide precursor film on a substrate by an appropriate technique, such as spray pyrolysis. Inorganic salts carry no extraneous hydrocarbon groups and we have found it easier to prepare dense and crack-free thick precursor films than is the case using organic salts, such as TFA. Next, the YBCO film is fluorinated by heat-treatment in an atmosphere containing a fluoride bearing gas. Finally, an epitaxial $YBa_2Cu_3O_7$ film is grown from the fluorinated precursor using a standard ex situ heat-treatment protocol. In this article we report on the details of this process as well as on the structural and superconducting properties of the resulting films.

2. Description of the spray-fluorination technique

A thermal spray pyrolysis technique, similar to that described in [11], was employed. Fig. 1 is a photograph of the spray pyrolysis apparatus used in this work. A fine mist of a Y–Ba–Cu nitrate salt solution in water was produced by ultrasonic excitation. The ultrasonic power source was an Ultraneb 2000 nebulizer operating at 2 MHz. Exposing the nebulizer directly to the Y–Ba–Cu nitrate salt solution resulted in the failure of the ultrasonic crystal. To remedy this the Y–Ba–Cu nitrate salt solution was contained in a custom built plastic vessel. The bottom of the vessel consisted of a 10 μm thick Mylar film and the vessel was mounted directly above the Ultraneb ultrasonic crystal. The vessel was coupled to the nebulizer using distilled water and the 10 μm thick Mylar film allowed the ultrasonic waves to propagate into the vessel producing a fine mist. The mist produced by the ultrasound was directed out of the vessel using a carrier gas. The gas used in the experiments described in this paper was air at a flow of about 10 l/min. A nozzle made of 18 mm pyrex tube directed the mist towards a heated substrate as shown in the photograph of Fig. 1. The substrate, a $3 \times 10\,mm^2$ $SrTiO_3$ single crystal, was attached to a metal block using silver paste. During spraying, the block was heated to a temperature of about 630 °C. As the impinging mist decomposed on the substrate a dense precursor oxide film formed on the surface of the substrate.

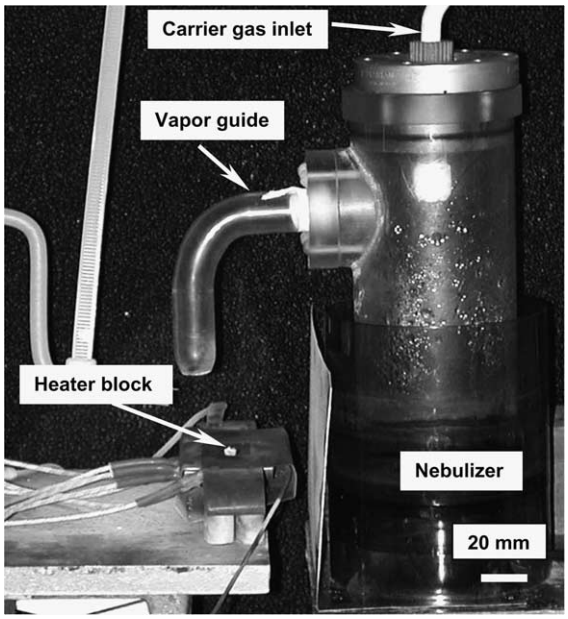

Fig. 1. Spray pyrolysis apparatus used to fabricate oxide precursor films.

The salt solution consisted of a mixture of Cu, Ba and Y nitrates in the composition ratio of Y:Ba:Cu = 1.0:2.0:0.5. The salts were dissolved in distilled water at a concentration of 0.01 M. The solution was purposely made off-stoichiometric as compared to the YBCO 1:2:3 stoichiometry in order to compensate for the different deposition rates of the constituent nitrates [12]. It is believed that the copper nitrate has a lower decomposition temperature and/or greater sticking coefficient, compared to the yttrium and barium nitrates, so the copper concentration was reduced accordingly. The Y:Ba:Cu stoichiometry of the sprayed precursor films was within 5% of the ideal 1:2:3 YBCO stoichiometry as determined by inductively coupled plasma (ICP) spectroscopy for films 1 μm thick. The vapor density during spraying was monitored using an infrared detection system. A deposition time of about 1 h and 20 ml of the solution were needed to deposit a 1 μm thick oxide precursor film.

The next step of our process is conversion of the as-deposited oxide precursor into a fluorinated oxide precursor. The oxide precursor is annealed in an atmosphere containing a fluorinated gas. The principle reaction involved is the transformation of BaO into fluorinated form. We have found that 1,1,1,2 tetrafluoroethane (CH_2FCF_3), a refrigerant (R-134a) used in modern automotive air-conditioning systems, serves perfectly as a source of fluorine. The precursor films were fluorinated in a tubular furnace in a partial vacuum in an atmosphere of 4 Torr of CH_2FCF_3 and 200 milliTorr of oxygen, at a temperature of 600 °C. We speculate that partial decomposition of the R-134a occurred at 600 °C releasing HF that we believe to be the fluorinating agent. Unfortunately, neither the degree of decomposition of the R-134a nor the partial pressure of HF could be determined. Analysis of the processing atmosphere by means of mass spectrometry did not revealed any presence of HF, nor was any substantial change in the mass spectrum of the processing atmosphere observed as the temperature of the furnace was raised from room temperature to 600 °C. This would indicate that the HF partial pressure was below 0.1 milliTorr, which was the detection limit of our gas sampling system. Two possibilities for this are: (i) neutralization of HF takes place en route to the spectrometer head, on metal vacuum tubing or the throttle valve, or (ii) the primary mechanism of HF release is catalytic decomposition of R-134a at the surface of the precursor, rather than bulk gas phase thermal decomposition. In the latter case, due to the small area of the film, there would be no substantial HF concentration in the processing atmosphere.

It was also discovered that the oxide films could be fluorinated by mixing some R-134a into the carrier gas that was used to transport the mist to the heated substrate. The results for only a single YBCO film fluorinated in this manner are presented in this paper, namely in Fig. 7, panel C.

The final step, after fluorination of the precursor oxide film, was conversion to epitaxial YBCO by partial vacuum ex situ heat treatment as described in [8]. The nominal atmosphere we employed was 40 Torr water vapor partial pressure, 100 milliTorr oxygen partial pressure, and a 735 °C processing temperature. The epitaxial film growth rate was ~0.2 nm/s.

3. Rate of fluorination reaction

To determine the rate of the fluorination process, several samples were quenched after a specified fluorination time had lapsed. Shown in Fig. 2 are

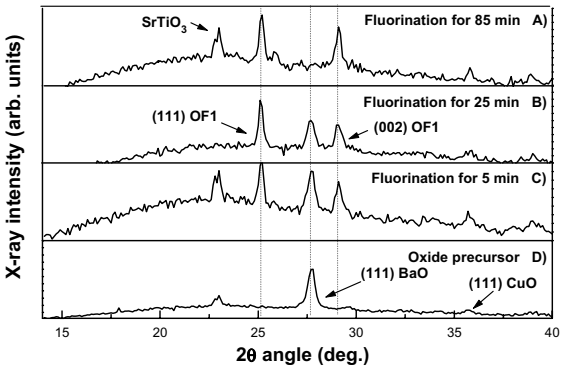

Fig. 2. θ–2θ XRD spectra of the oxide precursor at various stages of fluorination. The as-deposited sprayed precursor is shown in the panel D. The spectrum labeled 'Fluorination for 85 min' corresponds to a completely fluorinated film. The films were fluorinated at 600 °C.

the θ–2θ X-ray diffraction patterns of four samples 1 μm thick, three of which were fluorinated at 600 °C. The bottom spectrum, panel D, is that of an unfluorinated oxide precursor and the top pattern, panel A, is that of a completely fluorinated film. According to the XRD pattern, the as-deposited oxide precursor is a cubic modification of BaO [(1 1 1) reflection at $2\theta = 27.7°$] and CuO [(1 1 1) reflection at $2\theta = 36.1°$]. Yttrium oxide could not be detected by X-ray diffraction and is believed to be present in amorphous form. As shown in Fig. 2, during fluorination the BaO(1 1 1) peak at 27.7° decreases in intensity and is replaced by a cubic BaF_2-like oxy-fluoride, denoted OF1, with the strongest (1 1 1) reflection at $2\theta = 25.1°$. Note that it requires about 40 min to fluorinate a 1 μm thick film under these conditions. The fluorination rate was observed to increase by factor of 5 at a fluorination temperature 650 °C.

The oxy-fluoride phase is structurally similar to BaF_2 [9], i.e., it is cubic, with a lattice parameter $d = 0.61$ nm, somewhat smaller than that of BaF_2 for which $d = 0.62$ nm. The OF1 phase has a more compact unit cell because yttrium ions partially substitute for larger barium ions. This substitution is compensated by substitution of fluorine ions by oxygen ions and the resulting lattice parameter is almost identical to that of BaF_2. The OF1 phase was found to be identical to the oxy-fluoride phase found in precursor films made by vacuum co-evaporation of Y, Cu and BaF_2 [9].

Longer fluorination times resulted in the formation of another cubic oxy-fluoride phase, referred to as OF2, which has a smaller lattice parameter than OF1. Fig. 3 shows the XRD transformation of the OF1 phase, starting in panel D, to the OF2 phase, ending in panel A, for four films fluorinated for different times. The films were fluorinated at 600 °C in 4 Torr partial pressure of CH_2FCF_3 and 200 Torr partial pressure of oxygen. The OF2 phase is structurally similar to the OF1 phase but has a lattice parameter $d = 0.59$ nm. We assume that in the OF2 phase more oxygen sites are occupied by fluorine resulting in unit cell compression. The OF2 phase is stable at room temperature, however it releases fluorine and transforms back to the OF1 phase upon annealing in a fluorine-free oxidizing atmosphere. Due to this

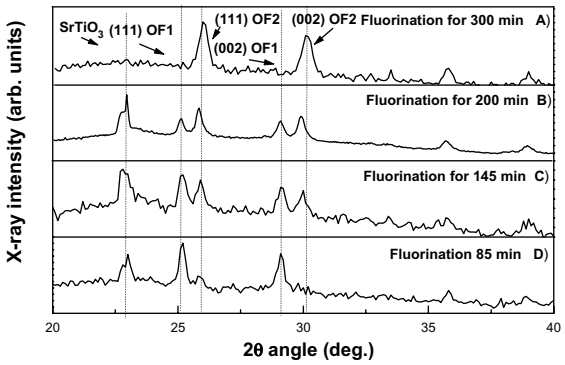

Fig. 3. θ–2θ XRD spectra showing the transformation of the OF1 oxy-fluoride phase to OF2 oxy-fluoride phase. The films were fluorinated at 600 °C.

effect, YBCO growth always starts from the OF1 phase. We did not observe OF2-YBCO conversion because by the time the sample is heated to over 700 °C the OF2 phase is completely oxidized to the OF1 phase.

The normalized intensities of the (1 1 1) peaks of the OF1 and OF2 phases ($2\theta \approx 25°$) were measured as a function of fluorination time. The normalized intensities for 1 and 3 μm thick films fluorinated at 600 °C at a partial pressure of 4 Torr of CH_2FCF_3 and 200 milliTorr oxygen is plotted in Fig. 4. The main conclusion is that for OF1 phase reaction time depends on the film thickness, which

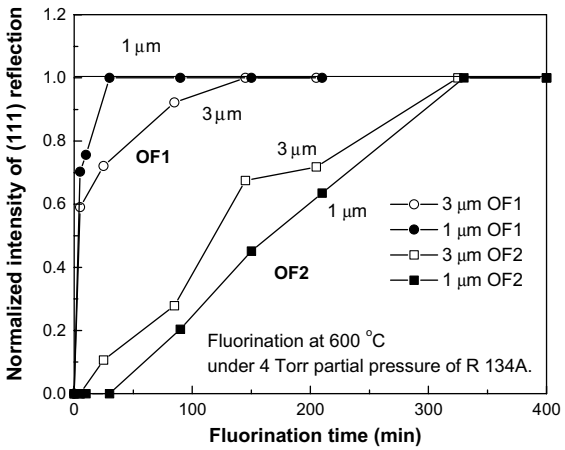

Fig. 4. Normalized intensity of (1 1 1) θ–2θ peak of the oxy-fluoride phases OF1 and OF2 in 1 and 3 μm thick films as a function of fluorination time.

implies that the fluorination rate is, to some extent, limited by diffusion of the CH_2FCF_3 gas or some other species, through the precursor solid. It seems that formation of the OF2 phase is less limited by solid state diffusion since there is little difference in reaction times for 1 and 3 μm thick films.

On a microscopic level, the un-fluorinated sprayed precursor appears as a mixture of nano-sized grains of BaO and CuO ≈ 10 nm in size as shown in the top panel of Fig. 5. Yttrium was not detected in the TEM diffraction pattern and is believed to be present in an amorphous form. The bottom TEM panel of Fig. 5 shows a film fluorinated at 600 °C for 30 min. In addition to the chemical transformation of Ba and Y into the OF1 phase, the film morphology also undergoes changes. Both films were 1 μm thick with a deposition time of ~1 h. Since the fluorination temperature was the same as the deposition temperature but for a shorter time, it is believed that the grain coarsening is due to the fluorination where the average grain size increases to 50 nm in the fluorinated sample as compared to a 10 nm grain size in the un-fluorinated sprayed precursor.

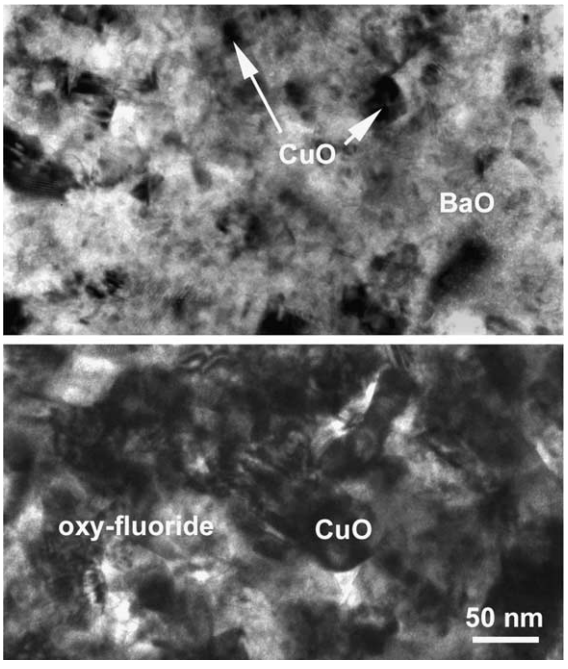

Fig. 5. TEM planar view microphotographs of an as-deposited un-fluorinated sprayed precursor, top panel, and a fluorinated sprayed precursor, bottom panel. The film in the bottom panel was fluorinated at 600 °C.

4. Growth and properties of YBCO from the fluorinated precursor

Using this spray pyrolysis technique, we have fabricated completely *c*-axis oriented YBCO films on $SrTiO_3$ and CeO_2 buffered $LaAlO_3$ substrates. Measuring in situ electrical conductivity of films during the heat treatment it was found that the kinetics of YBCO growth is the same as for vacuum-deposited precursor films [8]. This means that the HF-H_2O equilibrium constant is the same for both types of precursor. The degree of fluorination turned out to be important for the YBCO film quality. If a sample was not completely fluorinated, as evidenced by a BaO peak still being present in the XRD pattern, the resulting YBCO film had a large amount of random grains. We suggest that the BaO grains serve as sites for nucleation of randomly oriented YBCO.

The superconducting transition temperature for samples fabricated under optimal conditions was 91 K, zero DC resistivity (at a field criterion of 0.1 μV/cm). Unfortunately, the best superconducting critical currents for these samples were about one-half of that for vacuum-deposited films, i.e., 0.8 MA/cm^2 at 77 K and self-field for the best 1 μm thick sample. More typical J_c values were in 0.5 MA/cm^2 range. Such poor performance of these films was quite a surprise for us since the X-ray diffraction patterns appeared excellent with no sign of randomly oriented or *a*-oriented grains.

To understand the difference between YBCO films that were synthesized from sprayed and vacuum deposited precursors, we undertook a comparative study. In what follows, data on the properties of these YBCO films are compared. The fluorinated films were all 1 μm thick and were converted to epitaxial YBCO under identical conditions, 735 °C, 50 Torr water partial pressure and 100 milliTorr oxygen partial pressure.

(A) Spray-deposited epitaxial YBCO films tend to a have normal state resistance higher than is typical for good quality epitaxial YBCO films

deposited by vacuum deposition. Spray deposited films are in the range of 300–350 μΩcm at 300 K, compared with 250–280 μΩcm for a good quality *c*-axis oriented vacuum deposited film. This added resistivity elevates the whole $R(T)$ curve. For a film with a high critical current density, the extrapolated $R(T)$ curve is expected to have the value, $R = 0$ at $T = 0$. This is not the case for the spray deposited films presented here. If the ratio $R(300)/R(100)$ is used as a measure of the chemical or structural uniformity of the films, a uniform film should have a ratio of 3 or greater. For the best spray deposited films this ratio is below 2.8.

(B) Fig. 6 compares dc magnetization curves for vacuum deposited and sprayed samples. Magnetization measurement was done using a SQUID magnetometer in the zero-field cooled regime at 2 Oe dc magnetizing field. The broader magnetic transition in the temperature range of 30–80 K of the sprayed film indicates the presence of non-uniform superconducting regions.

(C) To search for compositional non-uniformity in the spray deposited films, a series of Raman spectra were taken at different points on the surface of the spray deposited film using a 6 μm diameter laser spot size as discussed in [13]. The Raman measurements revealed that some areas of this film contain Ba-rich domains. The YBCO

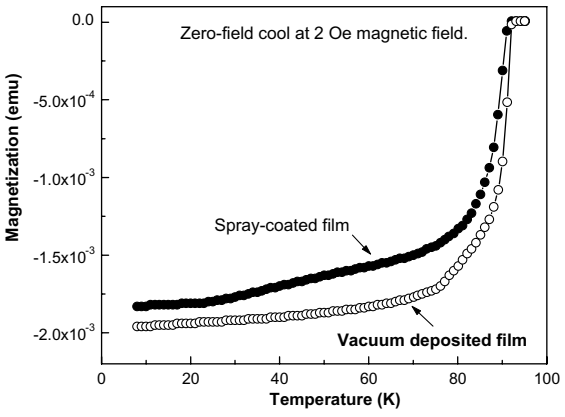

Fig. 6. Temperature dependence of the DC magnetization of epitaxial YBCO films fabricated from by vacuum deposition and spray pyrolysis. The applied magnetic field is perpendicular to the film surface.

in close proximity to these Ba-rich phases exhibits a high degree of cation disorder. In contrast, the spectrum of YBCO films formed from vacuum-deposited precursors contained only epitaxial YBCO lines, consistent with a single homogeneous YBCO phase.

Summarizing the above data, we conclude that spray-coated films have compositional inhomogeneity resulting in compositionally non-uniform YBCO films. This compositional inhomogeneity is presumed to be related to the details of the formation of the solid from the vapor. Using optical microscopy it was determined that droplets of the nitrate solution impinge upon the hot substrate, evaporate and leave behind a solid residue in the form of a pancake or "splat". We speculate that temperature gradients in the "splat" may lead composition inhomogeneity where the composition of the dried "splat" is nonuniform due primarily to the difference in the sticking coefficients of constituent nitrates. As noted previously, the overall film composition was determined by ICP, implying that the average composition of the "splats" was stoichiometric.

Another possible reason for the inferior performance of spray-deposited films is the texture of the oxy-fluoride. Precursors deposited by vacuum deposition and TFA and heat treated prior to formation of YBCO, exhibit strong (111) texture of the oxy-fluoride. That is, the oxy-fluoride is predominantly oriented so that the (111) plane is parallel to the plane of the substrate. A typical θ–2θ X-ray diffraction pattern of a vacuum deposited precursor heat treated at 600 °C is shown in panel A of Fig. 7. A very sharp (111) texture is in evidence in addition to a much weaker 002 reflection. X-ray diffraction patterns for two spray deposited precursors, fluorinated at 650 °C, are shown for comparison in panels B and C of Fig. 7, respectively. The spray deposited oxide precursor fluorinated at 650 °C in the normal manner (after deposition), panel B, has a stronger (00*l*) texture as indicated by the pronounced (002) peak of the oxy-fluoride. The spray deposited oxide precursor fluorinated during deposition at 650 °C, panel C, has an even more dominant cubic (00*l*) texture. Please note that this film was fluorinated by addition of small amount of R-134a to the

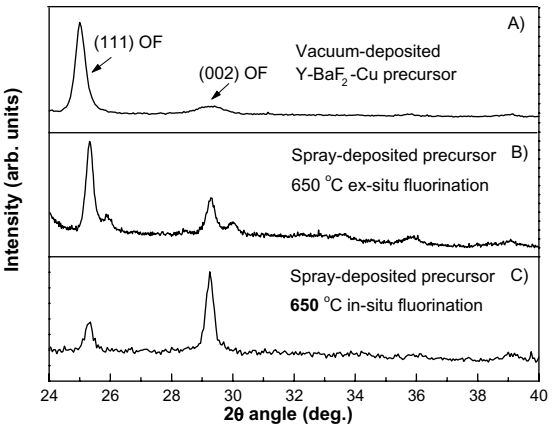

Fig. 7. Comparison of the θ–2θ XRD spectra of three films; a vacuum deposited YBCO oxide precursor film heat treated at 600 °C, panel A; a spray deposited precursor film fluorinated after deposition (ex situ) at 650 °C, panel B; and a spray deposited precursor film fluorinated during deposition (in situ) at 650 °C, panel C.

carrier gas during spraying of the aqueous nitrate solution.

A fluorinated precursor, prepared by vacuum deposition or TFA, with texture of the type shown in Fig. 7, panel A, can have a J_c well over 1 MA/cm^2. A film with the texture shown in panel B typically yields a J_c in the range 0.5–0.8 MA/cm^2. Finally, for films with the texture, as shown in panel C, J_c's exceeding 10^5 A/cm^2 could not be achieved. Transmission electron microscopy data obtained by us earlier also indicate, indirectly, that (1 1 1) texture may be crucial for *c*-axis nucleation [9,14]. This would suggest that films with a strong (1 1 1) texture are necessary to achieve high J_c YBCO films.

A direct test of this hypothesis requires the fabrication of spray coated precursor samples with a strong (1 1 1) oxy-fluoride texture. We estimate that this can be achieved by low-temperature fluorination of the oxide precursor in the 400–500 °C range. Unfortunately, it was not possible to test this hypothesis with our existing apparatus. The fluorination rate becomes negligible at temperatures below 550 °C, which is believed to be due to the low rate of CH_2FCF_3 decomposition.

Finally it should be noted that the (1 1 1) oxy-fluoride peak of the spray deposited films in panels B and C is shifted to higher angles as compared to the (1 1 1) oxy-fluoride peak of the vacuum deposited heat treated film of panel A. This is believed to be due to a difference in the oxy-fluoride compositions but its importance to achieving a high J_c is not presently known.

5. Conclusion

In conclusion we have presented a new technique using spray pyrolysis and gaseous fluorination for the fabrication of epitaxial YBCO films. This technique offers the potential of inexpensive scale-up for the production of coated YBCO conductors and thick YBCO films with relatively high critical currents. The fluorination of oxide films using a fluorine bearing gas can be applied and/or combined with many existing coating techniques for the production of thick *c*-axis oriented YBCO layers. The main difficulty with the process is believed to be either (i) the spatial variation of the film composition, which results in weak-link behavior, or (ii) the absence of a dominant (1 1 1) oxy-fluoride texture. More advanced spray coating technologies, utilizing a smaller droplet size may solve this problem.

References

[1] P.M. Mankiewich, J.H. Schofield, W.J. Skocpol, R.E. Howard, A.H. Dayem, E. Good, Appl. Phys. Lett. 51 (1987) 1753.
[2] A. Gupta, R. Jagannathan, E.I. Cooper, E.A. Geiss, J.I. Landman, B.E. Hussey, Appl. Phys. Lett. 53 (1988) 2077.
[3] M.W. Rupich, U. Schoop, D.T. Verebelyi, C. Thieme, W. Zhang, X. Li, T. Kodenkandath, N. Nguyen, E. Siegel, D. Buczek, J. Lynch, M. Jowett, E. Thompson, J.-S. Wang, J. Scudiere, A.P. Malozemoff, O. Li, A. Annavarapu, S. Cui, L. Fritzmeier, B. Adrich, C. Craven, F. Nui, R. Schwall, A. Goyal, M. Paranthaman, IEEE Trans. Appl. Supercond. 11 (2003) 2458.
[4] D.F. Lee, K.J. Leonard, L. Heatherly Jr., J. Yoo, F.A. List, N. Rutter, S.W. Cook, S. Sathyamurthy, M. Paranthaman, P.M. Martin, A. Goyal, D.M. Kroeger, Supercond. Sci. Technol. 17 (2004) 386.
[5] R. Feenstra, T.B. Lindemer, J.D. Budai, N.D. Galloway, J. Appl. Phys. 69 (1991) 6569;
R. Feenstra, D.K. Christen, J.D. Budai, S.J. Pennycook, D.P. Norton, H.H. Lowndes, C.E. Klanbunde, N.D.

Galloway, L. Correa (Eds.), Proc. of Sym. A-1 on High Temperature Superconducting Films, Inter. Conf. on Adv. Mater., North Holland, Amsterdam, 1991, p. 331.
[6] P.C. McIntre, M.J. Cima, M.F. Ng, J. Appl. Phys. 68 (1990) 4183.
[7] J.T. Dawley, P.G. Clem, M.P. Siegal, D.L. Overmyer, J. Mater. Res. 16 (2001) 13.
[8] V.F. Solovyov, H.J. Wiesmann, Li-jun Wu, M. Suenaga, R. Feenstra, Physica C 309 (1997) 269;
V.F. Solovyov, H. Wiesmann, Y. Zhu, L.-J. Wu, M. Suenaga, Appl. Phys. Lett. 76 (2000) 1911.
[9] L. Wu, Y. Zhu, V.F. Solovyov, H.J. Wiesmann, A.R. Moodenbaugh, R.L. Sabatini, M. Suenaga, J. Mater. Res. 16 (2001) 2869.
[10] M. Yoshizumi, I. Seleznev, M.J. Cima, Physica C 403 (2004) 191.
[11] J.L. MacManus-Driscoll, A. Ferreri, J.J. Wells, J.G.A. Nelstrop, Supercond. Sci. Technol. 14 (2001) 96.
[12] G.B. Blanchet, C.R. Fincher, Supercond. Sci. Technol. 4 (1991) 191.
[13] K. Venkataraman, A.J. Kropf, C.U. Segre, Q.X. Jia, A. Goyal, B.W. Wang, S. Chattopadhyay, H. You, V.A. Maroni, Physica C 402 (2004) 1;
K. Venkataraman, D.F. Lee, K. Leonard, L. Heatherly, S. Cook, M. Paranthaman, M. Mika, V.A. Maroni, Supercond. Sci. Technol. 17 (2004) 739.
[14] L. Wu, V.F. Solovyov, H.J. Wiesmann, Y. Zhu, M. Suenaga, Appl. Phys. Lett. 80 (2002) 419.